MODIFYING THE CRACK GROWTH IN A GLASS FIBER REINFORCED EPOXY BY ADDING POLYAMIDE 6 NANOFIBERS

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ABSTRACT

Recently, several types of nanoparticles are frequently incorporated in reinforced epoxy resin composites. Since it is difficult to obtain a homogeneous dispersion of these nanoparticles, the mechanical improvement of the composites is very moderate. Thermoplastic nanofibrous structures can overcome this issue. Therefore, this paper investigated the effect of electrospun polyamide 6 nanofibrous structures on the mechanical properties of a glass fiber/epoxy composite. The nanofibers are incorporated in the glass fiber/epoxy composite as stand-alone interlayered structures and directly spun on the glass fiber reinforcement. Both incorporation procedures have no negative effect on the impregnation of the epoxy. Incorporation of nanofibers increases the stress at failure in the 0°-direction, the best results are obtained when the nanofibers are directly electrospun on the glass fibers. Optical microscopic images also demonstrate that nanofibers prevent delamination when a 90° crack reaches a neighbourly 0° ply. When the composites are loaded under 45°, it is proven that for an identical stress, the glass fiber composite with deposited nanofibers has less cracks than when interlayered nanofibrous structures are incorporated.

INTRODUCTION

Owing to their light weight and high stiffness and strength, fiber reinforced epoxy resin composites are widely used in industry. However, an epoxy matrix is a brittle material, which could lead to unexpected failure of the composite. Thus, an improvement of the resin rich region between two plies with a different fiber orientation is recommended. Therefore, secondary (sub)micron reinforcements are often incorporated in the matrix.

Nanoparticles such as carbon nanotubes (CNT) and nanoclays can be added to the epoxy matrix to improve the mechanical properties of the matrix [1]. Due to their theoretical high stiffness and strength, CNT might improve the matrix characteristics [2]. However the overall improvement in mechanical properties such as stiffness and fracture toughness of the epoxy matrix is mostly very moderate [3,4]. The main disadvantage with these CNT's and nanoclays, besides the safety issues due to the small dimensions [5], is the difficulty to obtain a homogeneous dispersion of the nanoparticles in the resin [6]. Moreover, the viscosity of the resin increases significantly when nanoparticles are added. The toughness of a matrix can also be improved by incorporation of rubber particles or embedding thermoplastic inclusions [7]. But again, a homogeneous dispersion of the particles in the matrix is hard to obtain.

Thermoplastic nanofibrous structures offer a solution for the dispersion issue, since they can be readily embedded in the resin and incorporate a nanosized phase in the composite. These nanofibers also do not increase the viscosity of the resin. Furthermore, due to their macro

scale length, no health hazards are involved in the production and use of these nanofibers. Recent literature indicates that nanofibers contribute substantially to the ductility and fracture toughness of the composites [6]. This is related to the hypothesis that a secondary fibrous structure with a pronounced lower fiber diameter in addition to a primary fiber structure may increase several mechanical properties of composite materials [8].

This paper describes the effect of electrospun polyamide 6 (PA 6) nanofibrous structures on the mechanical properties of a glass fiber/epoxy composite. Therefore, the mechanical properties of a pure glass fiber composite are compared to glass fiber composites with added nanofibers. These nanofibrous structures are, on one hand, incorporated between the glass fabrics as stand-alone structures and, on the other hand, directly deposited onto the glass fabrics.

MATERIALS AND METHODS

All composite plates were reinforced with unidirectional E-glass fabric (Roviglas R17/475). In the fiber direction the reinforcement was 475 g/m², while in the perpendicular direction the reinforcement was 17 g/m². The matrix was EPIKOTE resin MGS RIMR 135 with EPIKURE curing agent MGS RIMH 137.

The composite plates were manufactured by vacuum assisted resin transfer moulding using a closed steel mould. The epoxy is first cured at room temperature for 24 hours and, thereafter, post cured for 15 hours at 80 °C. For all composite plates the stacking sequence was $[0°,90°]_{2s}$. The samples were cut to dimensions on a water-cooled diamond saw. All specimens had a thickness of 3.0 mm and a nominal width of 30 mm, as described in the ASTM D3039/D3039M-00. End tabs were used to avoid failure at the clamps.

The nanofibers were incorporated in the glass fiber/epoxy composites in two different ways. On one hand, they were inserted in between the various glass fiber mats as a stand-alone structure. On the other hand they were directly deposited on one side of the glass fiber reinforcement. Of course, also a reference composite without nanofibers was manufactured, to be able to investigate the improvement of the nanofiber addition.

For the fabrication of the nanofibers, 16 wt% PA 6 was dissolved in a 1:1 solution of 98-100 v% formic acid and 98 v% acetic acid. Both the polymer and solvents were obtained from Sigma-Aldrich and used as received. To obtain large uniform nanofibrous structures, the nanofibers were produced using a multi-nozzle electrospinning set-up. This multi-nozzle method, an in house developed technology [9], diverged from a mono-nozzle set-up only by the number of nozzles, the general methodology itself is identical. Ten nozzles, each fed by a syringe, were placed in two alternating rows in a plate which had a movement in the transverse direction. In the meantime, a grounded collector was moving in the longitudinal or production direction.

All nanofibrous nonwovens were spun in a conditioned room at 23 ± 2 °C and 50 ± 5 % RH. The tip-to-collector distance was 7 cm and the flow rate was set at 1.5 mL/h. The voltage was adapted until a stable process was achieved, this was between 25 and 30 kV. The stand-alone structures were electrospun directly on an aluminium foil, and afterwards released using water. For the deposited version the nanofibers were directly electrospun onto the glass fiber mats. The fiber diameter of the interlayered nanofibrous structures was 150 ± 19 nm, while for the deposited nanofibrous structures 230 ± 26 nm.

The tensile tests on the composites were performed on an electromechanical Instron 5800R machine with a load cell of 100 kN. The tests were displacement controlled with a speed of 2 mm/min and displacement, load, longitudinal and transverse strain, both measured with strain gauges, were recorded on the same time bases.

RESULTS AND DISCUSSION

IMPREGNATION OF THE EPOXY RESIN IN NANOFIBROUS STRUCTURES

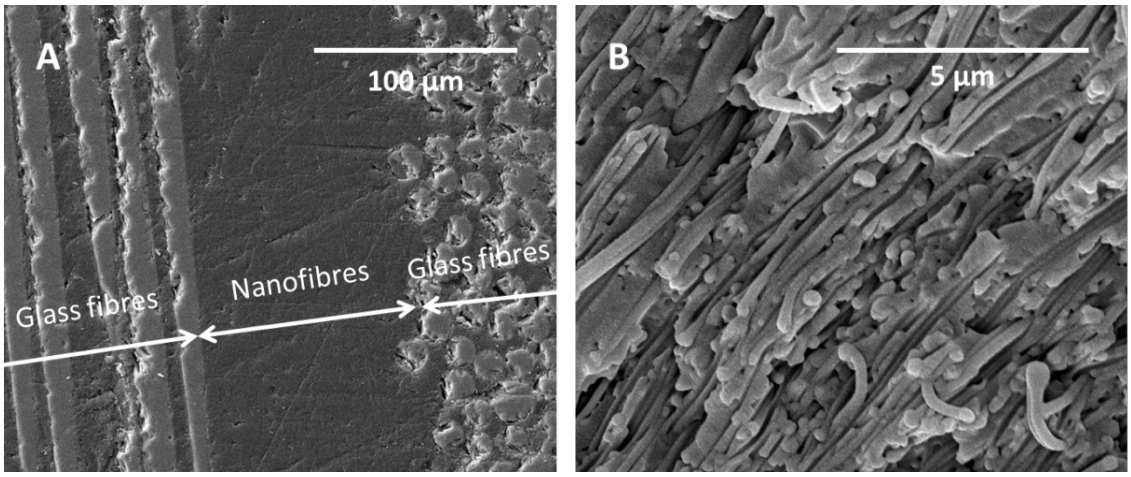

Figure 1: Cross section of the secondary nanofiber reinforced glass fiber composites (A.) and a zoom of the resin rich region filled with nanofibers between two plies with different fiber orientation (B.).

Before starting with tensile tests on the composite samples, it has to be investigated whether the reinforcements are well impregnated, especially the nanofibrous nonwovens. Nanofibrous nonwovens are structures with a high porosity, but also with very small pores, which can hinder the impregnation. Irregularities such as air bubbles could have a negative effect on the mechanical properties of the overall composite. The SEM images in Figure 1 show the good impregnation of the epoxy in both the glass fibers layer and polyamide nanofibers layer. Figure 1B demonstrates that the individual nanofibers were not damaged during the VARTM-process. Thus, the nanofiber layers have no disadvantages for the impregnation of the epoxy. This good contact between reinforcement and matrix is crucial for the load transfer from the composite to the reinforcement.

The dimensions of the resin rich region between two glass plies with different fiber orientation depend on the composition of the composite structure. The glass fiber composites without nanofibers had the smallest gap, only 13 ± 6.4 µm. Adding nanofibers in between the glass fiber layer causes an pronounced increase of this resin rich region between two glass fiber plies. Moreover, there also was a difference between the deposited and interlayered nanofibers, although the both structures had an identical thickness. The gap between two glass fiber layers for the deposited and interlayered secondary reinforced glass fibers composites was 36.4 ± 6.0 µm and 49.3 ± 7.5 µm, respectively. This increased space between the glass fiber plies has as a consequence that the nanofiber addition should be considered as extra separated plies.

MECHANICAL BEHAVIOR OF THE $[0°,90°]_{2S}$ STACKING SEQUENCE

Figure 2 proves the reproducibility of the specimens used in this research. As shown in the figure, the different stress strain curves with interlayered nanofibers coincide very well. The samples are obtained from different plates, indicated by the black and grey colour. So, it can be concluded that there is a good reproducibility between different composite plates, which was also the case for the other composite types. Therefore, it was chosen to show a representative curve of each composite type (GF: pure glass fibers; NF-I: interlayered nanofibers; NF-D: deposited nanofibers) in the following graphs.

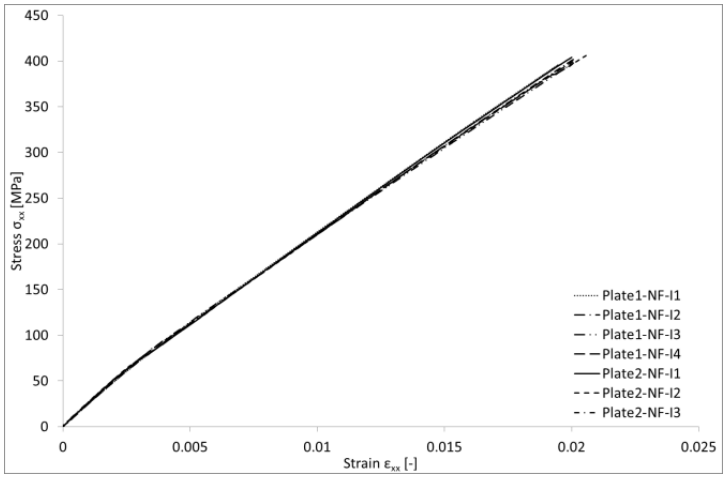

Figure 2: Reproducibility of the glass fiber/epoxy composites secondary reinforced with interlayered stand-alone nanofiber structures.

Since it was expected that the addition of nanofibers to the glass fiber composite would improve the mechanical properties, several tensile tests were performed. However, the stress-strain curves in Figure 3 do not directly show an improvement in the mechanical behaviour of the composite in the 0°-direction when nanofibers are added to in the glass fiber composites. In this 0°-direction the mechanical properties of the glass fibers are dominant compared to the ones of the thermoplastic nanofibers. Glass fibers have a lot higher strength and stiffness compared to the used PA 6 nanofibers. Furthermore, the stiffness of thermoplastic nanofibers is around 1 a 2 GPa [10], while the applied epoxy matrix has a stiffness of 3.37 ± 0.065 GPa.

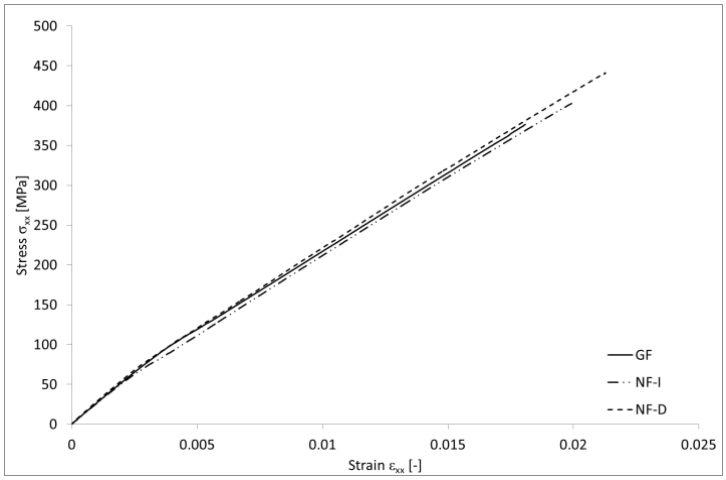

Figure 3: stress-strain curves of tensile experiments in the 0°-direction

The strain gauge signal was lost at about 2 % longitudinal strain, caused by debonding of the strain gauges, but the load signal was measured until failure. The first column of Table 1 gives the average stresses at failure of the three different composite types. All values are an average of five measurements. By adding interlayered nanofibers in between the glass fiber plies, the stress at failure increased from 550 MPa to 581 MPa. When the nanofibers are directly deposited onto the glass fibers the stress at failure increases further to 611 MPa. Thus, even though the mechanical properties of the nanofibers are inferior compared to the properties of the glass fibers, they improve pronouncedly the failure stress. It seems that the deposited nanofibers facilitate more the transfer of the load to the primary reinforcement. This can be understood by taking into account that there is a direct contact between the deposited nanofibers and glass fibers, which improves the load transfer to the glass fibers.

Table 1: Tensile properties of the different composite plates.

	Stress at failure [MPa]	Young's modulus [GPa]	Shear modulus [GPa]
Glass fiber composite	550 ± 16	26 ± 0.62	4.0 ± 0.36
Interlayered nanofibers	581 ± 13	26 ± 0.17	4.7 ± 0.30
Deposited nanofibers	611 ± 18	27 ± 0.64	4.7 ± 0.21

Indeed, Figure 4 clearly shows the difference in crack propagation between the glass fiber composites with and without PA 6 nanofibers. For glass fiber composites without nanofibers the 90° crack turns into a delamination when reaching a neighbour 0° ply, as illustrated in Figure 4.A. Thus, the structure delaminates. When PA 6 nanofibers are added, this delamination effect is much less explicit, see Figure 4.B. and C. So, it can be concluded that the nanofibers have a toughening effect in the resin rich region between the plies with different fiber orientation. This higher fracture toughness is in agreement with the research of Kim and Reneker about PBI nanofibers as reinforcement in an epoxy composite. [21].

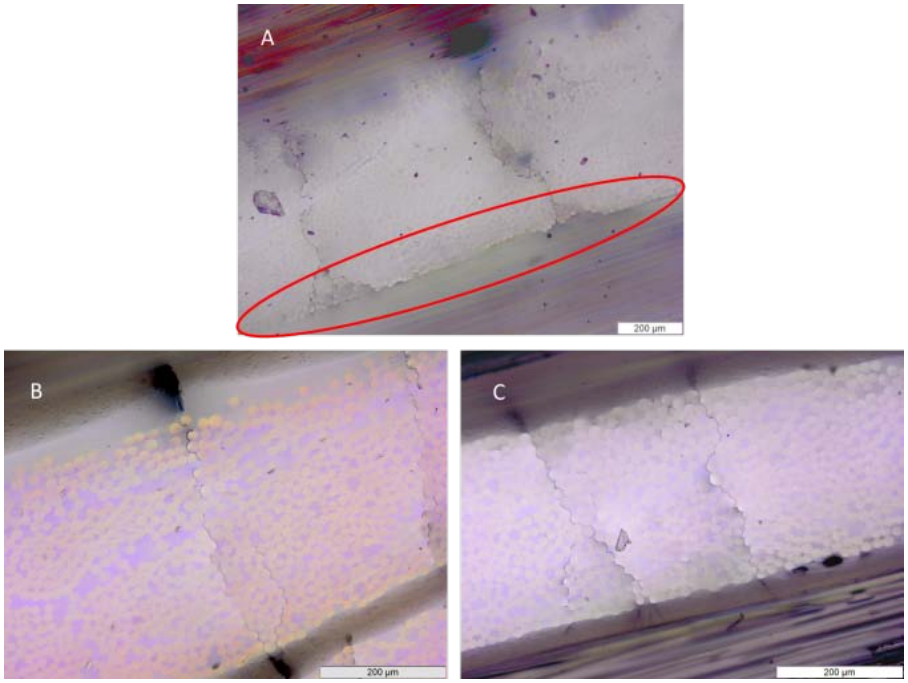

Figure 4: Optical microscopy images of the failed composites: deposited nanofibers (A.), interlayered nanofibers (B.) and pure glass fiber composite (C.)

Table 1 also gives the Young's modulus of the three different composite types, and it appears that there is no major increase of the stiffness when nanofibers are added to the glass fiber reinforcement. Since the stiffness of the composites is especially influenced through the reinforcement with the highest stiffness, it is logical that the stiffness does not increase significantly when PA 6 nanofibers are incorporated as a secondary reinforcement.

The Poisson's ratio of the several composite types also demonstrates that the effect of the incorporated PA 6 nanofibers is negligible, as can be noted from Figure 5. Because of the comparable stiffness of the resin and the PA 6 nanofibers, the latter have no pronounced effect on the dimensional properties of the composite.

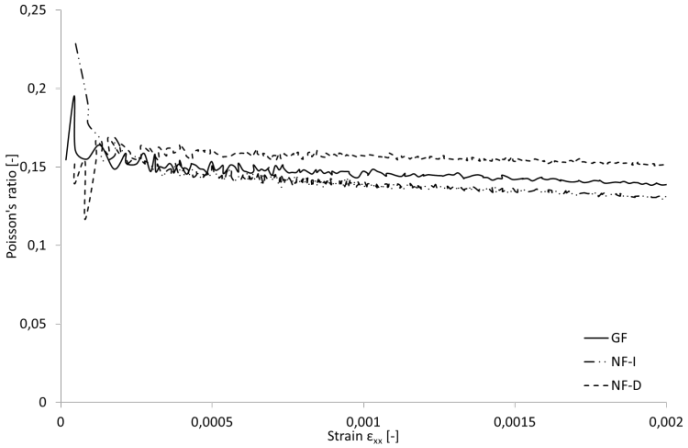

Figure 5: Evaluation of the Poisson's ratio ν_{xy} as function of the strain ε_{xx} for the $[0°,90°]_{2s}$ composites

MECHANICAL BEHAVIOUR OF THE $[+45°,-45°]_{2S}$ STACKING SEQUENCE

To further investigate the effect of nanofibers on the mechanical behaviour of glass fiber composites, tests under 45° are also performed. By testing the composites under 45° the mechanical properties of the glass fibers are less dominant compared to the other components. So, the advantages of nanofibers should be more pronounced. Figure 6 shows that for the same shear strain, the shear stress of the composites with nanofiber deposited on glass fibers is significantly higher than the glass fiber composites without nanofibers or with interlayered nanofiber mats. Thus, the deposited nanofibers facilitate the load transfer to the glass fibers, resulting in the higher shear stress. Since the interlayered nanofibers have no direct contact with the glass fibers, the load transfer to the fibers is not different from the plain glass fiber/epoxy composite hence there is no improvement in shear stress.

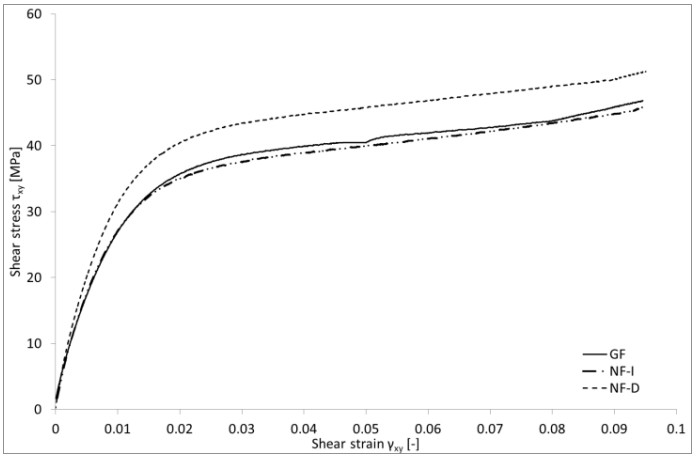

Figure 6: Evaluation of the shear stress τ_{xy} as a function of the shear strain γ_{xx} for the $[-45°,+45°]_{2s}$ composites

Figure 7 shows some optical microscopic images of samples with interlayered and deposited PA 6 nanofibers loaded to 40 MPa and then unloaded. 40 MPa was chosen since this was the end of the linear behaviour of the composited with interlayered nanofibers. From the optical microscopic images it is clear that the interlayered samples have many more cracks in the glass plies compared to the glass fiber composite with deposited nanofibers. This is in agreement with the curves in Figure 6. It can thus be concluded that the deposited nanofibers transfers the load much better tot the primary glass fiber reinforcement.

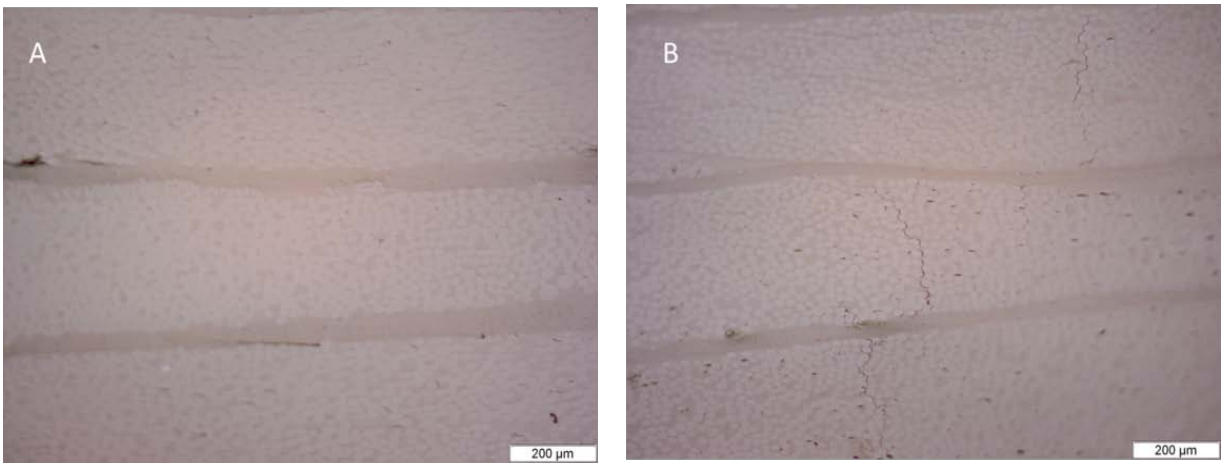

Figure 7: Optical microscopy images of composites with deposited nanofibers (A.) and interlayered nanofibers (B.) at a stress of 40 MPa

The shear moduli of the three different composite types are also noted in Table 1. It is demonstrated that the shear moduli of glass fiber composites with nanofibers are higher compared to the ordinary glass fiber composite.

CONCLUSION

The addition of nanofibers to the glass fiber/epoxy composite has no negative influence on the impregnation of the epoxy in the several types of reinforcements. However, nanofibers affect the resin rich region between the plies with different fiber orientation. The largest gap increase is found for the interlayered nanofibers.

The incorporation of polyamide 6 nanofibrous structures in the $[0°,90°]_{2s}$-composite increases the stress at failure, deposited nanofibers are slightly better than the interlayered nanofibrous structures. It is found that nanofibers prevent or minimize the formation of delamination cracks between two glass fiber plies.

The tensile experiments under 45° also demonstrate that the deposited nanofibers facilitate the load transfer to the glass fibers. Optical microscopic images show that at 40 MPa an interlayered nanofiber reinforced glass fiber composite has much more cracks than a deposited one. Thus, it can be concluded that deposited nanofibers improve significant some mechanical properties of a glass fiber composite.

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